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Characterisation of the ONERA / CNES High Performance Green Monopropellants Towards a Thruster Application

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This paper describes the evolution of surface tension of three green monopropellants according to temperature to facilitate the design of a green monopropellant thruster prototype. During the testing, reactions with some of the materials in contact with these monopropellants have been observed leading to a material compatibility testing (60°C for 10 days). Finally, a preliminary testing of the combustion of an isolated droplet and a monopropellant atomisation have been made and filmed to begin the visualisation of the phenomena taking place.

I. Nomenclature

I_{sp}	=	Specific impulse
OB	=	Oxygen balance
On	=	Ohnesorge number
We	=	Weber number
We_c	=	Critical Weber number

II. Introduction

HYDRAZINE is a compound widely used in the Attitude and Orbit Control System (AOCS) of spacecraft. However, while it has been known for more than a century and used as a propellant since the Second World War [1], its hazardous nature casts an evergrowing shadow on its hegemony as a propellant in satellite propulsion [2, 3]. Indeed, in 2011, the European Union regulation of Registration, Evaluation, Authorisation and restriction of CHemicals (REACH) has designated hydrazine as a substance of very high concern [4] therefore endangering its production, importation and use on the European soil and thus challenging the European space industry. Consequently, in 2016, the *Centre National d'Etudes Spatiales* (CNES) and the *Office National d'Etudes et de Recherches Aerospatiales* (ONERA) signed a research collaboration agreement to develop a Green MonoPropellant (GMP) that would replace hydrazine whilst showing improved performances, low toxicity and high versatility [5]. Amongst the numerous monopropellants that were imagined in the early stages of this project [6], only a few currently remain after the first selection that has been made (toxicity, feasibility, cost, safety of synthesis, handling and use, etc.).

In this article, we review the latest findings of the selection of the few remaining monopropellant candidates. At first we will focus on the study of the surface tension of the different Ionic Liquids (ILs) and more specifically, survey its evolution with regards to temperature. This will grant us a good insight into the potential atomisation performance of the three candidates and thus, indirectly give us a hint about their combustion performance when used in a thruster.

Secondly, we will inspect the results of the material compatibility testing that was conducted following signs of reaction between certain monopropellants and one of the elements that have been used to measure the surface tension of

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these GMPs. This analysis participated into the elimination of an IL candidate as it critically reacted with a recurrently used spacecraft material.

Finally, we will perform a preliminary study to verify whether an atomisation in the best case scenario is indeed possible - atomisation that will then be followed by the combustion of an isolated droplet. The analysis of these tests will allow us to discuss of the future ways with which the research on these GMPs will be lead in the near future.

III. Surface Tension

A. Rationale and Objectives

One of the key objectives of the CNES-ONERA project is to design a green monopropellant thruster prototype to guide the optimisation and conception of a future flight-ready engine. Such process requires experimental knowledge of the different phenomena present during the atomisation, ignition and steady combustion of the green monopropellant. Alas, due to the ionic liquid nature and the novelty of the three candidates - named CNES03, CNES05 and ID25 - current numerical simulations and models lack field results to guide us, from both a performance and a security point of view, leaving us with no choice but to proceed iteratively and with precaution.

However, and to help us designing our prototype, notably by achieving an atomisation of good quality, we will utilise the work of Robert S. Brodkey in his "Phenomena of Fluid Motions" (ed. Addison-Wesley, 1969) in which he described the notion of a critical Weber number (shown in Eq. (1) [7]) below which breakup does not occur.

$$We_c = 12(1 + 1.077On^{1.6}) \quad (1)$$

As written in the subsequent works of M. Pilch and C. A. Erdman in "Use of Breakup Time Data and Velocity History Data to Predict the Maximum Size of Stable Fragments for Acceleration-Induced Breakup of a Liquid Drop" (International Journal of Multiphase Flow, 1987), this critical Weber number would then be compared to the Weber number of the flow. Should We be inferior to We_c , atomisation would be highly improbable. On the contrary, should We_c be inferior to We , we could witness drop breakup following the mechanisms shown by Pilch and Erdman in Fig. 1.

In order to calculate this critical Weber number, we need to know the surface tension of the few remaining GMPs which is the main objective, along with the knowledge acquired per se, of the study of the surface tension of the ILs as detailed below. It should nonetheless be noted that while this analysis is only valid for Newtonian fluids, the evaluation of the Newtonian nature of our monopropellants is still to be done. However, even if the results show that our GMPs are non-Newtonian, the surface tensions measured will still be relevant in an effort to attain and optimise a fine atomisation.

B. Caveats

1. Prerequisite

Before performing this experiment, it should be noted that more than a hundred tests have been conducted on water. These experiments had three objectives:

- 1) Train the experimenter to handle the tensiometer as this experiment relies heavily on the preparation of the equipment.
- 2) Clean thoroughly the probe and the brass base to get rid of any impurity that would greatly influence the results.
- 3) Create a database of surface tension values for water and verify that they are in accordance with the CRC Handbook of Chemistry and Physics [9] that is used as a reference.

In the graph used to summarise some of the tests and compare them with the reference, (i.e. Fig. 2), we can see that, whilst the surface tension measured is satisfying for temperatures ranging from 10°C to 30°C, the tests systematically indicate values above the reference for higher temperatures. We believe that this effect comes solely from the evaporation. Indeed, as a test assessing the surface tension of water at 80°C shows us (cf. Fig. 3) it seems that the upper surface of water is progressively distorted as the test unfolds according to the mechanic described in the following paragraph.

In Fig. 3, once the contact between the probe and the surface has been made (A), the measured value of surface tension starts to rapidly climb (B), (C) and (D). This increase seems to be induced by evaporation as this phenomenon causes a deformation of the surface which in turn and by the ever-growing tension of the free surface, pulls the probe thus increasing the surface tension measured. We can also note that the surface tension reaches a maximum (D), before decreasing (E). It appears to be linked to the fact that - as evaporation becomes too important - the surface of water still

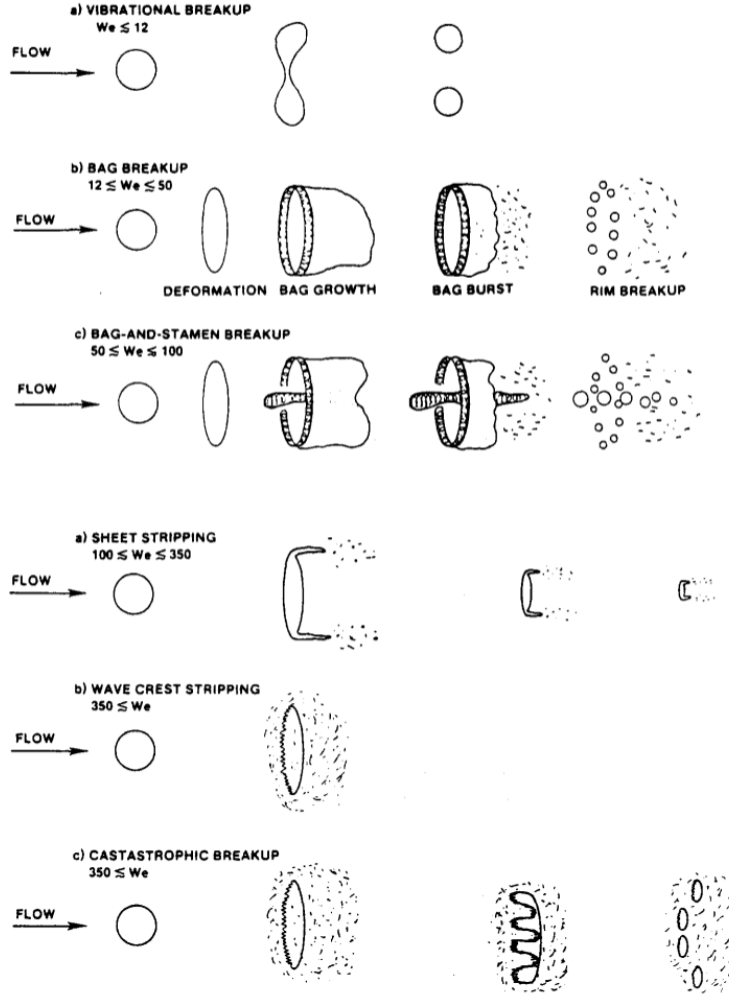


Fig. 1 Breakup mechanisms [8]

in contact with the probe decreases. Finally, when the tension connecting the string of water to the probe becomes overwhelming, this link snaps (F), causing the value measured to suddenly plummet and remain at zero (G).

2. Validation Interval

On top of the evaporation phenomenon discussed in the previous paragraph, we have to take into account the measurement noise and its induced result variation. Indeed, during our experiments on water, we have noted that the weight seen by the probe varies constantly between +0.2 mg and -0.2 mg which we will define as our measurement noise. We have also noted that a difference of 0.1 mg translates to a surface tension variation of 0.16 mN/m.

Moreover, and at the very start of a test, the precision scale of the tensiometer is tared which, due to the measurement noise mentioned in the previous paragraph, can lead to an offset of the weight read of plus or minus 0.2 mg as can be seen in Fig. 4. Because of this, the weight read by the tensiometer *when no effort is applied* can range from -0.4 mg (if the scale has been tared when the noise was at its maximum) to +0.4 mg (if the scale was tared when the noise was at its minimum). This means that for a given weight value, and without any information regarding the taring moment and supposing a perfect preparation and measure, we can only guarantee the veracity of this value plus or minus 0.4 mg - a global variation of 0.8 mg. Knowing that we cannot distinguish scale imprecision from real variation of surface tension should this variation be inferior to 0.8 mg, we decide to set a value that will be of use for the validation of our tests : the validation interval. This validation interval will have a value in mN/m corresponding to a variation of 0.8 mg, i.e.

$$0.16 \times \frac{0.8}{0.1} = \boxed{1.28mN/m}$$

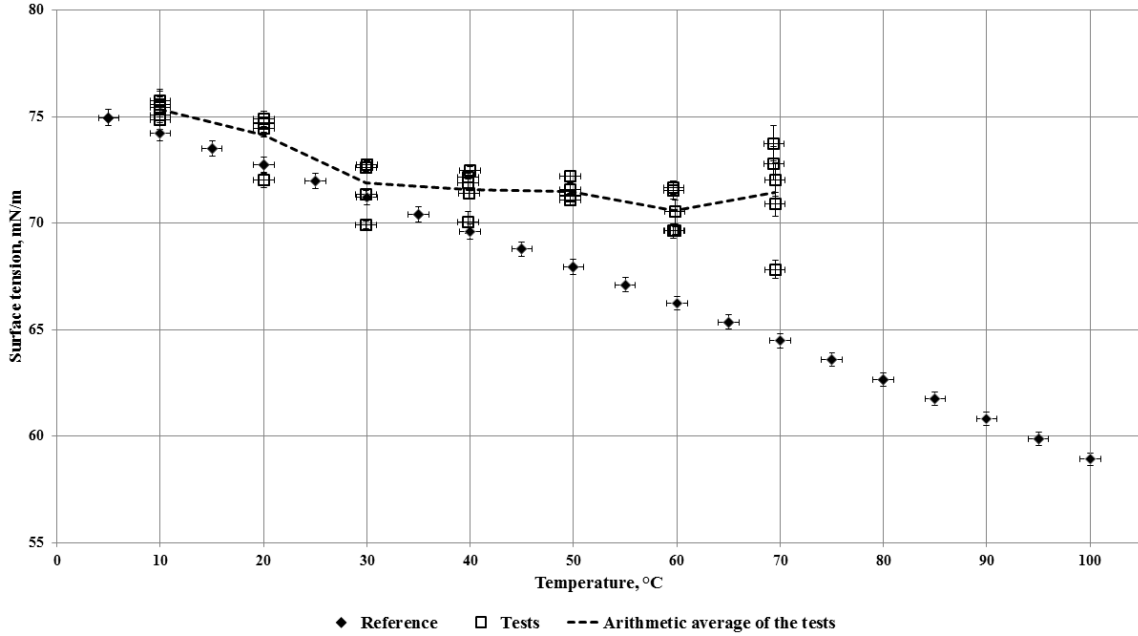


Fig. 2 Evolution of the measured surface tension of water and comparison with the reference [9]

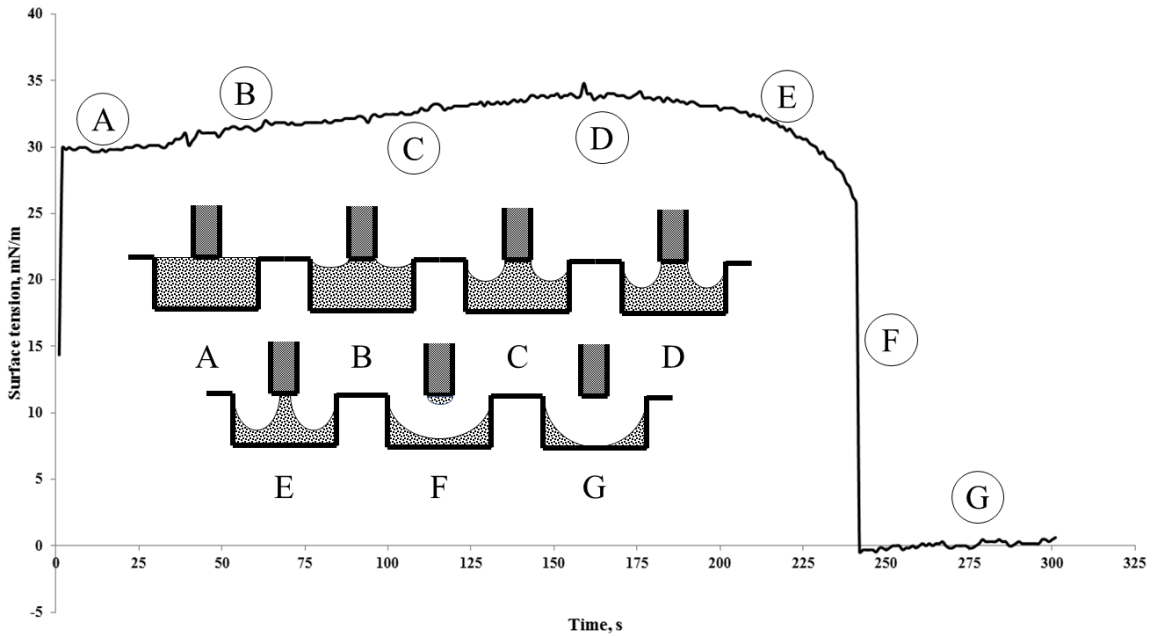


Fig. 3 Evolution of the measured surface tension of water at 80°C and apparent geometry of the upper surface. Note that the values in this graph are NOT to be taken as they are as this figure is shown to illustrate the suspected behaviour causing the divergence between the tests and the reference in Fig. 2 rather than providing reliable numerical results.

3. Validation

As the surface tension of our green monopropellants have never been tested, we do not know whether a test has gone correctly or not until we have a high number of different measures to compare it with. As the tensiometer requires both to be handled with care and to be constantly clean, requirements that can only be checked after the test, and as we do possess a limited supply of monopropellant - meaning that each test must be as reliable as possible - we need a method

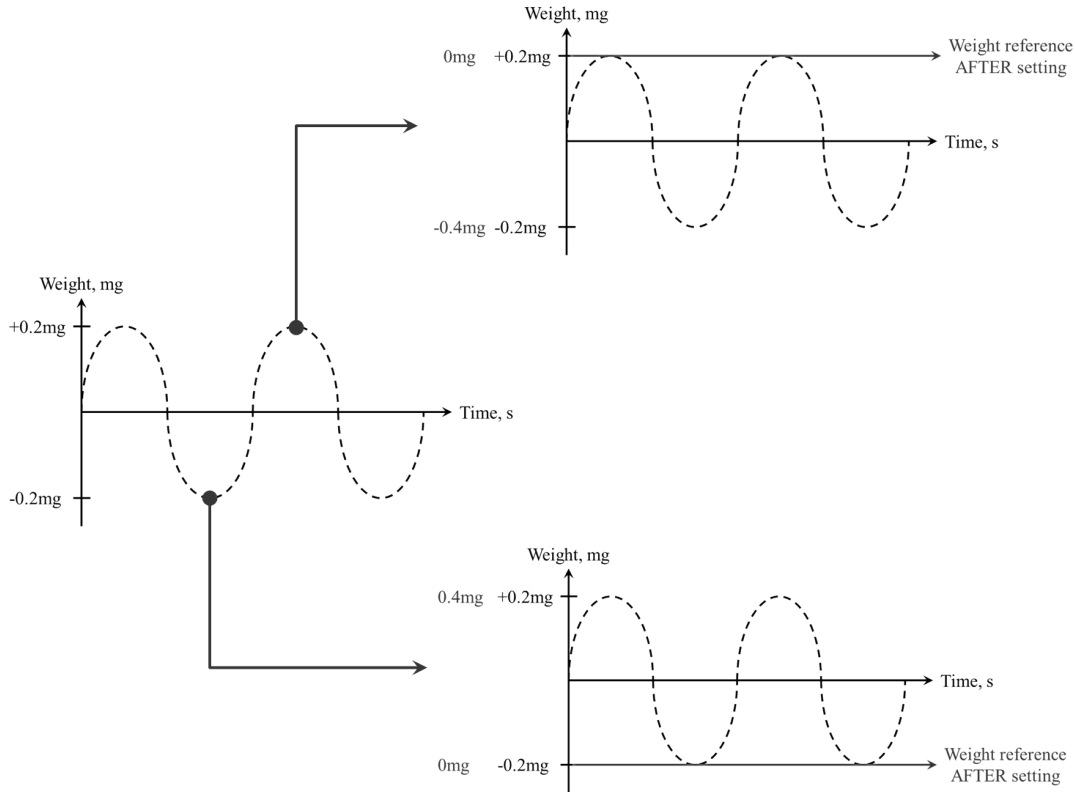


Fig. 4 Impact of the setting instant on the weight values read by the tensiometer.

to prepare the experiment that would give us a satisfying amount of trust *before* the test. In order to do so, we imposed two validation criteria (*Accuracy* and *Precision*) which definitions are found in the list below.

Accuracy

Here we want to be sure that the values measured are close to the real value. In order to do so, we decided to perform two tests on water before each test on a GMP. These two preliminary tests serve a dual purpose as they, first, allow - along with the cleaning procedure - to evacuate any dust or monopropellant in order to make the tests independent, and second, serve as quality control before each live test. This quality control is thus made with the fluid with which we have the most experience, i.e. water. Also, as evaporation on water only becomes significant for temperatures higher than 30°C (according to Fig. 2), we will have two validation rules for the accuracy depending on the temperature. For temperatures up to 30°C: For a test on monopropellant to be considered as accurate, its two preliminary tests on water must return values equal to the value of the reference [9] plus or minus one validation interval. For temperatures above 30°C: For a test to be considered as accurate, its two preliminary tests on water must return values that are included within the range of surface tension delimited by the reference (minimum) and the arithmetic mean of our database (maximum) (cf. Fig. 2) plus or minus one validation interval.

Precision

For a given run of tests, we want to be able to tell whether a deviation from the mean of the run is only due to the intrinsic error of the tensiometer or if another phenomenon is causing it. In order to do so, and for each run, we will compare the results of the run and the mean of the run. For a run to be considered as precise, the tests that comprise it must be within one validation interval from the arithmetic mean of the run.

C. Method for a Single test

1. Equipment

The tensiometer used is a Kruss force tensiometer K-100 placed in a room maintained at 20°C. The tensiometer uses a Kruss platinum probe PL03 and a custom brass receptacle (cf. Fig. 5). Temperature setting is made via a Lauda

thermostat Loop L100 and the measure of temperature is made by inserting a thermocouple into the custom receptacle along with a small amount of vacuum grease for thermal contact.

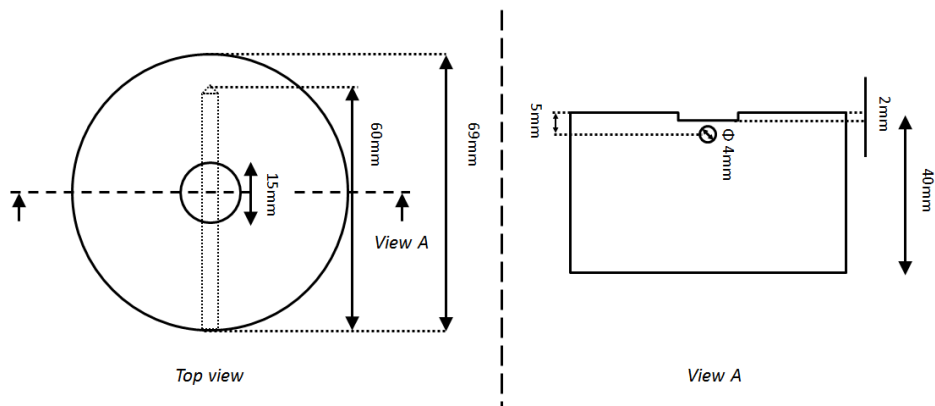


Fig. 5 Blueprint of the custom brass receptacle. Note the blind hole of 4mm of diameter used for temperature measuring that passes right below the vessel receiving the tested fluid.

2. Procedure

Before each test, the receptacle and the rod are *thoroughly* washed with isopropanol and a fibre-free cloth. They are then dried with a heat gun as we could not follow the instructions from Kruss that consisted in the heating of the probe with a blowtorch until the thick end becomes red because of the pyrotechnical classification of the zone we are operating in. The probe and receptacle are then placed in the tensiometer and a thermocouple is inserted in the receptacle. Once the temperature is as desired and steady, the test liquid is then carefully placed in the vessel and the volume of fluid is adjusted until the free surface is as flat as possible. Finally, the receptacle is brought up until the free surface is at about 2 mm from the probe.

The automated process then starts: the probe switches from the safety to the measuring position and the tensiometer proceeds to the taring. Then, the receptacle is slowly risen (2 mm/min) until the fluid surface is detected by the probe. Once done, the measure begins and stops either because it has reached its objectives (50 consecutive points with a standard deviation of 0.15 mN/m) or its time out (300 s). These objectives were tuned to reject any sample that would see its surface tension ever so slightly change during the test. At the end of the test, the probe switches back to its safety position, the receptacle is moved down and the test fluid (should it seem unaltered) is retrieved for other applications that do not require precision (e.g. valve and injection testing).

D. Results

1. ID25

Table 1 Surface tension of ID25 at 20°C.

Test number	Test accurate?	Surface tension (mN/m)	Standard deviation (mN/m)	Half confidence interval 95% (mN/m)	Fluid temperature upon contact (°C)
1	True	60.39	0.14	0.28	20.0
2	True	61.97	0.15	0.30	19.9
3	True	55.15	0.24	0.48	20.0
4	True	51.08	0.18	0.36	20.0
5	True	58.81	0.15	0.30	20.0
Mean surface tension of ID25 at 20°C: 57.48 mN/m					

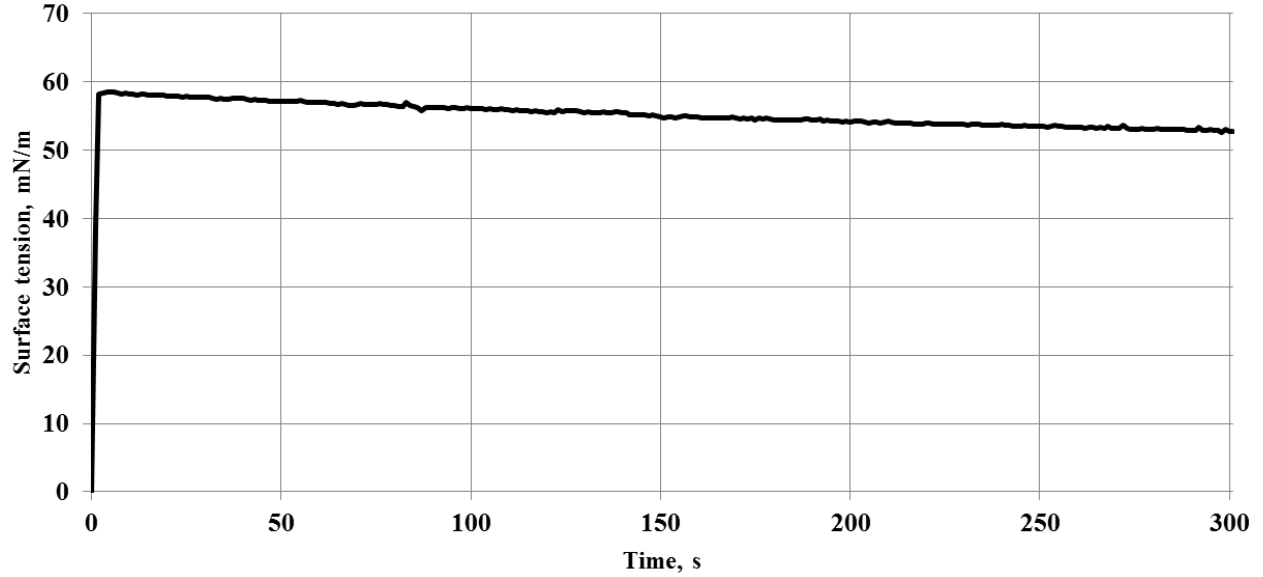


Fig. 6 Evolution of the surface tension of ID25 at 40°C. Sampling frequency: 1Hz.

2. CNES03

Table 2 Surface tension of CNES03 at 20°C.

Test number	Test accurate?	Surface tension (mN/m)	Standard deviation (mN/m)	Half confidence interval 95% (mN/m)	Fluid temperature upon contact (°C)
1	True	72.79	0.14	0.28	20.0
2	True	73.17	0.13	0.26	20.0
3	True	72.90	0.13	0.26	20.0
4	True	74.11	0.15	0.30	19.9
5	True	74.31	0.15	0.30	20.0
Mean surface tension of CNES03 at 20°C: 73.46 mN/m					

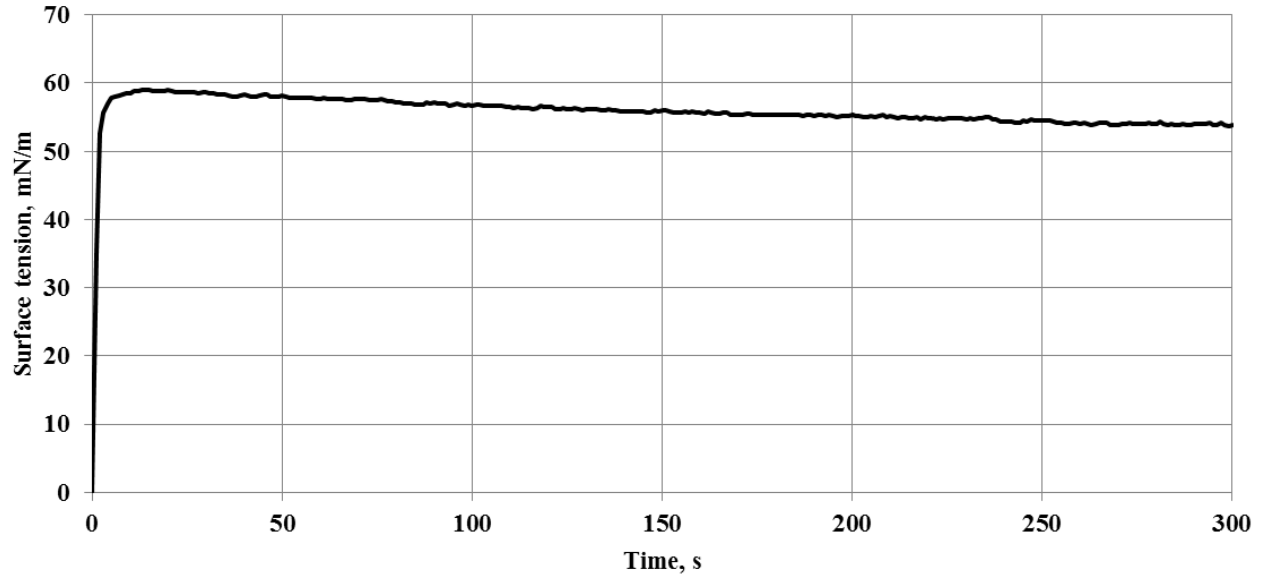
Table 3 Surface tension of CNES03 at 30°C.

Test number	Test accurate?	Surface tension (mN/m)	Standard deviation (mN/m)	Half confidence interval 95% (mN/m)	Fluid temperature upon contact (°C)
1	True	73.43	0.14	0.28	30.5
2	True	73.63	0.15	0.30	30.5
3	True	72.59	0.13	0.26	30.5
4	True	73.39	0.15	0.30	30.6
5	True	73.70	0.13	0.26	30.6
Mean surface tension of CNES03 at 30°C: 73.35 mN/m					

Table 4 Surface tension of CNES03 at 40°C.

Test number	Test accurate?	Surface tension (mN/m)	Standard deviation (mN/m)	Half confidence interval 95% (mN/m)	Fluid temperature upon contact (°C)
1	True	70.63	0.13	0.26	40.3
2	True	69.57	0.15	0.30	40.3
3*	True	57.59	0.11	0.22	40.1
4	True	69.28	0.15	0.30	40.3
5	True	66.26	0.14	0.28	40.2

Mean surface tension of CNES03 at 40°C: 68.94 mN/m

**Fig. 7 Evolution of the surface tension of CNES03 at 50°C. Sampling frequency: 1Hz.**

3. CNES05

Table 5 Surface tension of CNES05 at 20°C.

Test number	Test accurate?	Surface tension (mN/m)	Standard deviation (mN/m)	Half confidence interval 95% (mN/m)	Fluid temperature upon contact (°C)
1	True	60.48	0.14	0.28	20.0
2	True	60.37	0.15	0.30	19.9
3	True	60.36	0.15	0.30	20.0
4	True	60.90	0.14	0.28	20.0
5	True	60.54	0.12	0.24	20.0

Mean surface tension of CNES05 at 20°C: 60.53 mN/m

*This test shows a surface tension value that is much lower than what would be expected based on the other tests of the same run. The cause of this has been determined a posteriori. It appears that during the experimental preparation, too much CNES03 has been inserted in the vessel which caused the upper free surface to be slightly curved up. This curve has reduced the weight of the probe seen by the precision scale by *lifting* it up and has thus also reduced the resulting surface tension. This test will therefore not be taken into account during the rest of the article.

Table 6 Surface tension of CNES05 at 30°C.

Test number	Test accurate?	Surface tension (mN/m)	Standard deviation (mN/m)	Half confidence interval 95% (mN/m)	Fluid temperature upon contact (°C)
1	True	60.20	0.13	0.26	30.5
2	True	60.04	0.15	0.30	30.6
3	True	60.25	0.14	0.28	30.5
4	True	60.07	0.14	0.28	30.6
5	True	60.04	0.14	0.28	30.6

Mean surface tension of CNES05 at 30°C: 60.12 mN/m

Table 7 Surface tension of CNES05 at 40°C.

Test number	Test accurate?	Surface tension (mN/m)	Standard deviation (mN/m)	Half confidence interval 95% (mN/m)	Fluid temperature upon contact (°C)
1	True	59.56	0.13	0.26	40.3
2	True	58.98	0.10	0.20	40.3
3	True	59.30	0.15	0.30	40.4
4	True	58.79	0.12	0.24	40.1
5	True	58.79	0.12	0.24	40.1

Mean surface tension of CNES05 at 40°C: 59.08 mN/m

Table 8 Surface tension of CNES05 at 50°C.

Test number	Test accurate?	Surface tension (mN/m)	Standard deviation (mN/m)	Half confidence interval 95% (mN/m)	Fluid temperature upon contact (°C)
1	True	57.36	0.14	0.28	50.1

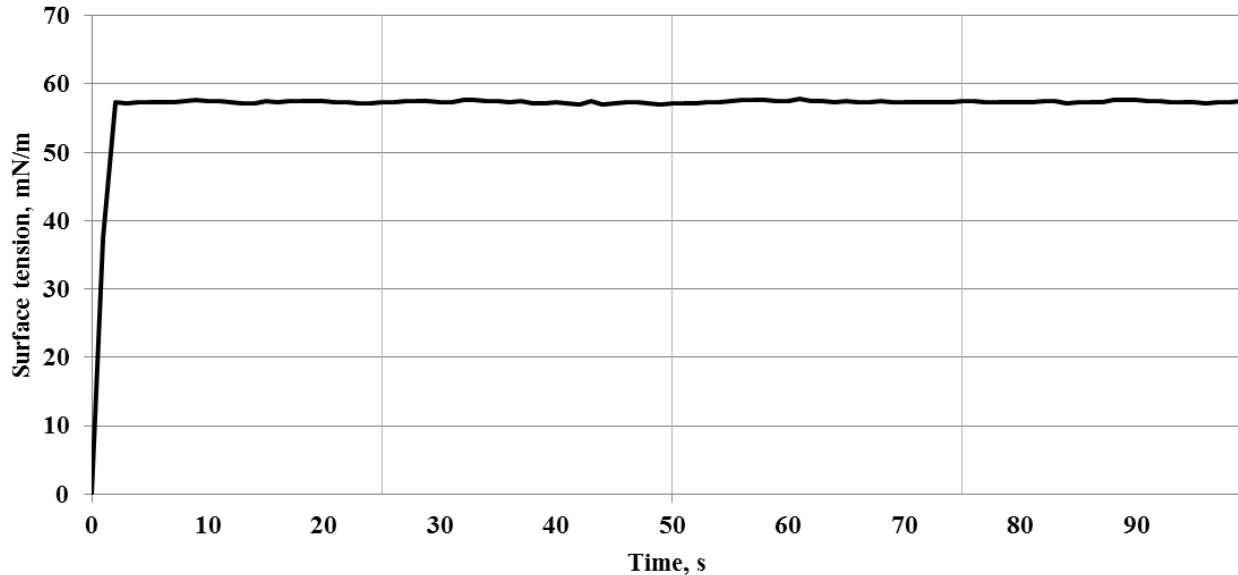


Fig. 8 Evolution of the surface tension of CNES05 at 50°C. Sampling frequency: 1Hz.

E. Discussion

1. ID25

With high suspicions concerning a potential reaction with the brass-made receptacle, ID25 is currently the only monopropellant (from our candidates) to have been tested for a single temperature. Given the result discrepancy at 20°C (cf. Fig. 9), it does not appear sensible to go beyond and run tests at 30°C as, should this wide range of results be linked to a reaction, an increase of temperature would also increase the discrepancy and the risks of a decomposition in the tensiometer - which would result in a catastrophic failure. We can also argue that further tests, at 30°C for example, would deplete our already limited ID25 supply without guaranteeing significant results.

However, in order to have an insight on the different mechanisms that take place during a test with ID25 and to infirm the hypothesis according to which the variation in the results were solely due to a badly executed experimental preparation - which would thus induce a static error on the surface tension -, we have decided to run under high surveillance a single (and *accurate*) test on ID25 at 40°C. This temperature has been chosen to accentuate the potential effects taking place at 20°C.

As can be seen in Fig. 6, a notable effect is actively modifying the surface tension of ID25 as the test proceeds. This effect, while not being easily visible on tests at 20°C (should we disregard the timeouts and barely achieved standard deviation objectives during this run), may be the direct cause of the wide variation of surface tension. In this hypothesis, the experiment preparation has a direct effect but in a matter of *when* rather than *how*. Indeed, and should we take Fig. 6 as an example, the value of surface tension decreases by approximately 10% in just 5 minutes.

As this type of error cannot be linked to an improper experiment preparation and as no evaporation could explain this variation due to the very nature of ID25[†], we suppose that a plausible explanation would be that ID25 reacts with the brass-made receptacle (cf. Fig. 5). To put this hypothesis to the test, we have performed a rapid material compatibility test that can be found in section IV.

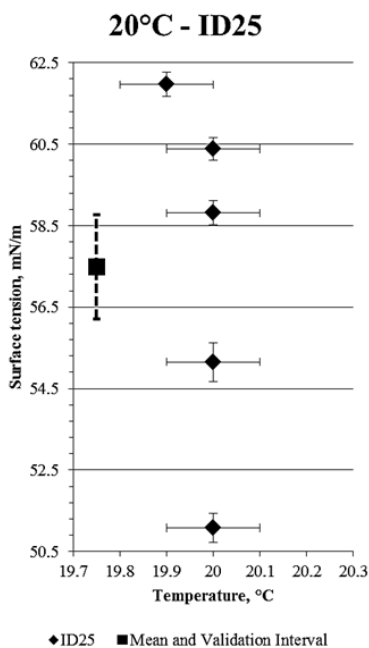


Fig. 9 Summary of the surface tension results on ID25 at 20°C.

[†]ID25, CNES03 and CNES05 are all ILs possessing an extremely low vapor pressure and are, as such, not prone to evaporation.

2. CNES03

As for ID25, we highly suspect CNES03 to react with the brass-made receptacle used for the measure of surface tension (cf. Fig. 5). Indeed, we find once more a certain discrepancy through the tests of a single run - may it be at 40°C (cf. Fig. 10) instead of 20°C as was the case with ID25. Again, and in order to gain insight on the same hypothesis made for ID25 (reaction with brass), we carried out a similar test by performing a single (and *accurate*) test on CNES03 at 50°C. This temperature has been chosen to accentuate the potential effects taking place at 40°C whilst trying to keep the risks at an acceptable level.

It appears once again that instead of finding a constant value - that would indicate an improper experimental set up - we can clearly see in Fig. 7 that the surface tension is continuously decreasing; a behaviour similar to that of ID25 that hints us towards a reaction with brass. Consequently, and to test this hypothesis, we have also performed a material compatibility test which results can be found in section IV.

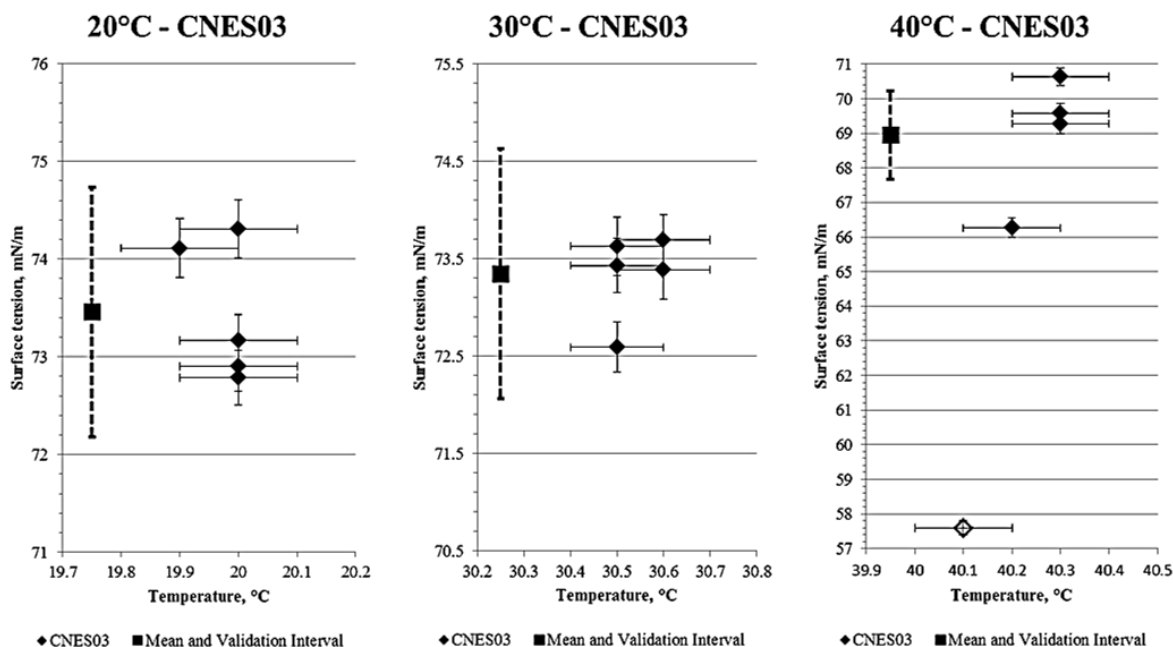


Fig. 10 Summary of the surface tension results on CNES03 at 20°C, 30°C and 40°C. Note that the third test of the 40°C run (hollow diamond) is not taken into account as its value has been greatly influenced by a badly executed experimental preparation.

3. CNES05

As it can be seen from Figs. 8 and 11, CNES05 does not seem to react with the receptacle or go through any visible decomposition process while being in contact with brass and being heated at temperatures ranging from 20°C to 50°C. This confidence in the stability of CNES05 comes from the regularity with which the tests of a run are largely included within the validation interval - which was not the case with ID25 and CNES03. Moreover, no visible variation of the surface tension can be seen on Fig. 8 which may indicate that the temperature of future potential tests could be increased to 60°C - and even perhaps 70°C - without causing a decomposition. Finally, and although no reaction has been detected, CNES05 will also go through a rapid material compatibility test to compare it to the other GMPs.

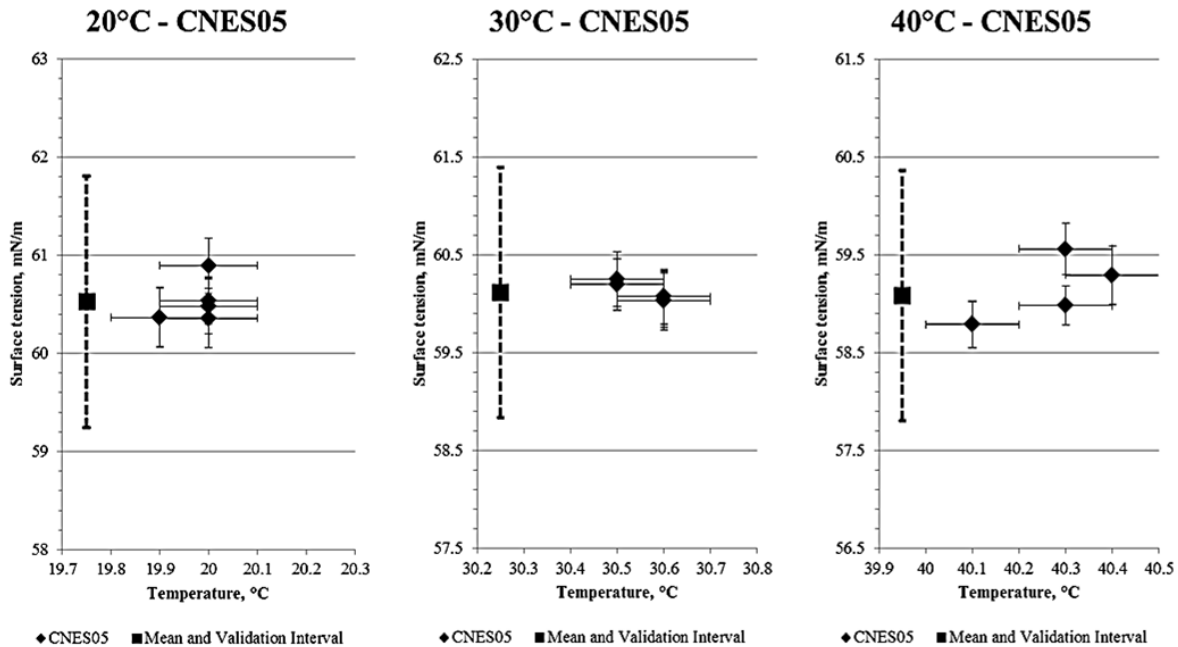


Fig. 11 Summary of the surface tension results on CNES05 at 20°C, 30°C and 40°C.

4. Summary

By using the information obtained in this section, we can plot, in Fig. 12, a graph that summarises the results obtained. As expected, the surface tension of CNES03 plummets between 30°C and 40°C which - given Fig. 10 - seems to come from the beginning of a reaction with the brass-made receptacle. A contrario, given the apparent absence of reaction between CNES05 and brass or temperature, this GMP sees its surface tension decline steadily as indicated by the Pearson correlation coefficient of approximately 0.93.

It should be noted that a linear correlation is searched by default for two reasons: first, our reference for water from [9] fits perfectly with this type of correlation and second, the only GMP tested that has been both accurate and precise from 20°C to 50°C without showing any signs of reaction - i.e. CNES05 - also fits correctly with a linear regression. We can suppose that the slight curvature of the surface tension of CNES05 is directly caused by the increasing temperature. Furthermore, and by supposing that CNES03 and ID25 both react with brass, these ILs may see their surface tension decrease because brass acts as a catalyst *instead* of acting as a mere reagent; The fall of surface tension for ID25 and CNES03 might therefore solely be due to a rise of the temperature in these monopropellants which would mean that the values shown in Fig. 12 for CNES03 and ID25 are the surface tension of a decomposing GMP. In this case, the values of surface tension for CNES03 at 40°C and ID25 at 20°C could still be used for the pre-design of a thruster as these values would correspond to a GMP that has begun its decomposition but has not yet burned.

Should we focus on ID25, it would not seem unreasonable to make an analogy with CNES03 as a first approximation. Indeed, in Fig. 10, the tests made with CNES03 at 40°C are, for their majority, beyond the validation interval; Let us also remember that this validation interval allows us to make the difference between a fluctuation due to the tensiometer and a true variation of the surface tension according to our definitions. When the temperature rose from 30°C to 40°C, the surface tension of CNES03 decreased by 6%. If we suppose that a stronger phenomenon is taking place with ID25 at 20°C - as not a single test is within the validation interval of the run - and supposing a linear relation, it would mean that the true value of surface tension for ID25 at 20°C is *at least* 6% higher than the value measured - i.e. higher than 61 mN/m.

Finally, it now appears primordial to conduct material compatibility tests to confirm or infirm the theory according to which CNES03 and ID25 react catalytically with brass. Moreover, and given the surface tension runs performed, CNES05 appears to be the best GMP of the three candidates examined because of its low surface tension (approximately 15% lower than water at 20°C) and its apparent stability. In the second place comes CNES03 followed by ID25 which - while presenting better performances (Isp and OB) than its counterparts - suffers from an apparent strong incompatibility with certain materials and a high production cost.

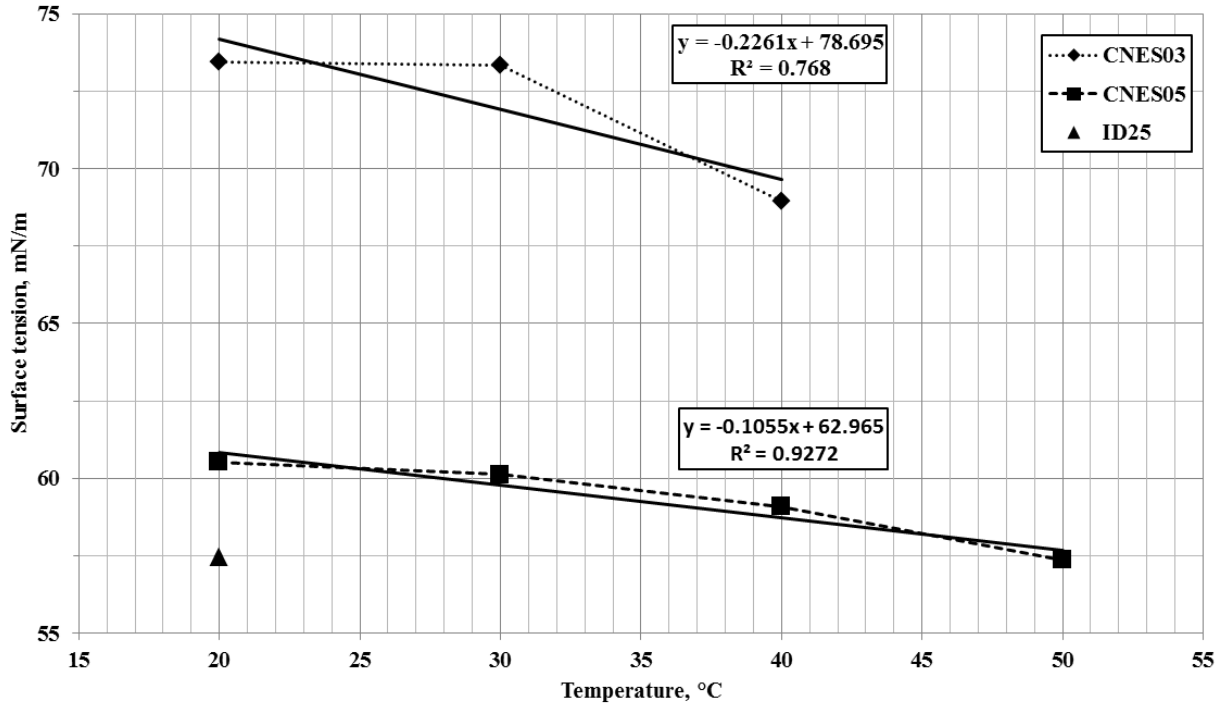


Fig. 12 Summary of the surface tension results for ID25, CNES03 and CNES05 for temperatures ranging from 20°C to 50°C and their associated trend lines (solid lines). Note that the points represented here are the arithmetic means of the runs that have been shown in Figs. 9, 10, 11 and Table 8.

IV. Material compatibility

A. Rationale and Objectives

We have seen in section III that there might have been a reaction when using our brass-made receptacle with CNES03 and ID25 during the surface tension tests. Confirming or infirming this hypothesis, in itself, justifies the realisation of a material compatibility testing. Nevertheless, this experiment would truly bear its fruits should a material currently used in space be tested - e.g. stainless steel. It is thus for these two reasons - explaining the behaviour during the surface tension runs and testing the reaction of the three GMP candidates with space-used materials - that this material compatibility trial will be performed on the three ILs (CNES03, CNES05 and ID25) and in three configurations (no material added, brass and stainless steel). However, given the limited supply of monopropellant and time that can be allocated to this experiment, the objective of this material compatibility test will be to check whether severe incompatibilities - i.e. rapid reactions instead of accelerated aging for long durations - exist between the aforementioned monopropellants and materials.

B. Method

A stainless steel block perforated by nine blind holes has been manufactured to contain nine samples. Each sample is put in a vial and then closed by a rubber balloon (with colors identifying the monopropellant). The configurations tested are detailed in Table 9. Given the fact that we do not know the activation energy of the different monopropellants and as this trial is performed to know whether a monopropellant reacts relatively quickly with a given material, we arbitrarily decide that the test will consist in keeping the samples at 60°C during a period of 10 days. To keep this temperature, the perforated block mentioned above containing the vials will be heated in a water bath that regulates automatically its level to compensate for the losses caused by evaporation.

Table 9 Configurations tested for the compatibility trial.

	CNES03 10 drops (blue balloon)	CNES05 10 drops (yellow balloon)	ID25 10 drops (pink balloon)
Nothing added with the monopropellant	Configuration 1	Configuration 2	Configuration 3
Brass (powder, 1 gram)	Configuration 4	Configuration 5	Configuration 6
Stainless Steel (1x1x0.5mm chip, 1 gram)	Configuration 7	Configuration 8	Configuration 9

C. Results

First of all and at the very end of the test, not a single balloon had its base - i.e. its part attached to the vial - intact. Indeed, and even for the vials only containing monopropellant, the rubber at these places appeared extremely weakened and cracked. Two hypotheses can be formulated: either the monopropellants have started to decompose even though their decomposition temperatures are above 100°C, or the balloons have simply been greatly affected by the combination of both the stress and heat sustained. However, and as the cracks appear both inside and outside the balloons, it would seem that the monopropellants only played a small role, if any, in the degradation of the rubber.

More importantly, out of the nine different configurations, four reacted, among which two completely decomposed. The first decomposition happened with configuration 6 before the vials could be placed in the heating bath (i.e. approximately 3 minutes after adding the monopropellant to the material). The second decomposition was undertaken by configuration 4 approximately 3 minutes after the vials had been placed in the heating bath. Regarding configuration 9, although the mix did not decompose, it appeared - at the end of the trial - that ID25 changed its color, from a translucent lime green to an opaque brown; It should be noted that the ID25 from configuration 3 did not change its color, thus implying a reaction with stainless steel. Finally, even though it is unknown whether this effect really comes from a reaction between brass and CNES05, approximately a fourth of the brass powder contained in configuration 5 agglomerated and could not be taken out of the vial. More observations on these configurations are written in Table 10 and seen in Figs. 13 and 14.



Fig. 13 From left to right: Vials and mixtures of the configurations 4, 5, 6 and 9. Note the lump of brass visible in the vial of the configuration 5.

D. Discussion

First, and as we expected from the surface tension experiment, brass reacts strongly with ID25 and CNES03. We can also note that the rapidity of the reaction (3 minutes at 20°C for ID25 and 3 minutes at 60°C for CNES03) represents correctly what had been found in Figs. 9 and 10 as CNES03 had to be in contact with brass at a higher temperature before reacting. Moreover, we can insist on the severity of the incompatibility between ID25 and brass as even at room temperature, this monopropellant begins its decomposition. On a sidenote, let us also point out that an exploratory test during which we deposited ID25 and CNES03 on platinum chips at room temperature to check whether this material could be used as a catalyst did not show a severity similar to the one obtained with brass as no visible decomposition nor increase in heat has been seen. Furthermore, the greenish dust that can be seen on the configurations 4 and 6 in Fig.14 might indicate the presence of copper oxide that would infirm the eventuality of a catalytic reaction developed in the

Table 10 Observations on the samples that have reacted during the trial. Note that while all the balloons were sticky and easily deformable after the trial, a few stood out and are therefore mentioned as such in this table.

Configuration	Observations Vial	Observations Balloon	Observations Mixture
Configuration 4	Interior of the vial appears darker than before the trial and entirely covered with the mixture described in the last column.	Balloon sticky and fragile suggesting contact with a very hot fluid. Interior of the balloon covered with a dark coating among which figures a greenish powder reminiscent of copper oxide.	Among the pile of light golden brass powder can be found a few dark grains. It should be noted that the powder seems completely dry.
Configuration 5	The vial does not seem different than a new one.	The balloon has a texture and resistance close to the ones of configurations 1 to 3.	As for configuration 4, a few darker grains are found in the brass. Moreover, almost a fourth of the brass powder has agglomerated in the vial. Its aspect is solid, as if the powder had started to fuse into a lump of molten brass.
Configuration 6	Identical to configuration 4.	Similar to configuration 4 but with a balloon that is even more fragile and stickier.	Identical to configuration 4.
Configuration 9	The vial does not seem different than a new one.	The balloon has a texture and resistance close to the ones of configurations 1 to 3.	Stainless steel chips covered with a brown opaque fluid that can only originate from a reaction with ID25.

summary of section III to favour instead the role of the brass as a pure reagent in an oxidation.

Second, we can remark that, although the balloon and vial of the configuration 5 do not stand out from the ones of configuration 2, the mixture appears to be wet and darker than the configurations 4 and 6. Furthermore, a notable portion of the brass powder has agglomerated into a small solid that could not be brought out of the vial. This leads us to the conclusion that a reaction between brass and CNES05 does exist but is infinitely less severe than that of CNES03 and ID25. Also, and even if the mechanism behind this reaction is yet unknown, it will not be researched in this article as the determination of the nature of the reactions is not part of the objectives of this experiment. Nonetheless, we can still remember that the decrease in the surface tension of CNES05 with increasing temperatures did not perfectly follow a linear relation as it showed a slight concave nature (cf. Fig. 12). In the light of the material compatibility experiment, this increasingly decreasing surface tension might now be explained by this apparent yet limited reaction between brass and CNES05.

Third, and as we expected from the surface tension run with ID25, this monopropellant is completely incompatible with brass, reacting within mere minutes after being mixed with this material and kept at room temperature. Moreover, this GMP has also shown signs of reaction with stainless steel as can be seen in Table 10 and Fig. 13. This last incompatibility makes it almost unusable in a spacecraft application which is why the characteristics and performances of ID25 will not be investigated any further.

Finally, this material compatibility trial allowed us to answer the major questions that emerged from the surface tension experiment despite its limited nature (*only* 10 days at 60°C). It did show that ID25 was not suitable to our application due to its incompatibility with stainless steel. Nonetheless, CNES03 and CNES05 both seem good candidates for carrying on the atomisation and ignition tests with a preference for CNES05 because of its better material compatibility and lower surface tension. In the tests to come, CNES03 will therefore be used for calibrations and experimental set-up - which will also allow our CNES05 supply to last longer -, and CNES05 will henceforth be the GMP on which our efforts will be focused on.



Fig. 14 Overview of the balloons used during the trial. The balloons are in the same order as the configurations of Table 9 - e.g. upper row, from left to right : configurations 1, 2 and 3.

V. First Atomisation and Combustion

A. Rationale and Objectives

The surface tension and material compatibility trials have allowed us to confirm that only two of the three candidates - with a preference for CNES05 - were fit to be taken to the next phase of our tests: atomisation without combustion and droplet ignition. Indeed, now that these trials have been carried out, we know that the remaining GMPs *should* have the potential to be atomised and may not pose a risk to the fluidic system put in place. We would like to emphasise on the *should* as CNES03 and CNES05 are both ionic liquids and their characteristics may vary, for example, depending on the speed of the fluid and thus, on the conditions of the atomisation.

The objective of this section is therefore to prove - under *reasonable* conditions - whether our IL candidates can be atomised and if their droplets can burn. In order to realise this capability demonstration, the experiments set up aimed to answer by a simple yes or no without any regard for the quality of the atomisation or ignition. Indeed, and should the GMPs be capable of atomisation and ignition, these tests will guide us towards a more elaborate - and thus, more qualitative - experimental set-up. A contrario, these preliminary tests will have represented a certain economy of equipment, personnel and monopropellant.

B. Equipment and Method

1. Atomisation

The atomiser is a single orifice (0.1 mm diameter) nozzle capable of theoretically delivering 0.3 mL/s at an optimum pressure of 60 bar. This technical solution has been chosen due to its adequation with our injection requirements and its low cost of replacement - no flight-ready nozzle has been used as the results that it would provide in this preliminary test do not counterbalance the increased cost. Concerning the feeding system, it is a micro-fluidic network filled and pressurised with monopropellant by a syringe capable of delivering a maximum pressure of 220 bar. The exiting GMP is

filmed with a high-speed camera and a backlight. The procedure in itself is as simple as could be done: the high-speed camera associated to the backlight starts recording the exit of the nozzle after which the syringe pressurises the - already filled - network with monopropellant and makes it go through the atomiser at a determined pressure.

2. Ignition

The ignition system consists of a thick copper plate perforated longitudinally through its centre in which is placed the hot extremity of a glow plug. We have shown in preliminary testing that this combination allows us to reach at least 500°C on a flat copper surface. Concerning the droplet, it is created by using a fine plastic eyedropper approximately 50 cm above the hot surface and then falls until it impacts the copper. We can estimate that the volume of monopropellant impacting the surface is of roughly the same size as a water droplet - which has a volume of 0.050 mL. The impact and ignition is filmed with the conjunction of a high-speed camera and a backlight. The process is, once more, made as simple as we could: the glow plug heats the copper plate and when the temperature has reached its maximum value, the backlight is lit, the high-speed camera starts recording and, finally, a single drop of monopropellant is released from the eyedropper to impact on the hot plate.

C. Results

1. Atomisation

In order to prove the atomisation capabilities of our GMPs, we have decided to conduct two tests: the first concerning the transient state - obtained by filming a pulse -, and the second, the steady state. In Fig. 15, we can therefore see the results through those different states of an injection at 40 bar using the nozzle described above. We can observe that the development of the spray meets the usual steps of a classic atomisation: first comes a solid stream with the generation of a droplet train (a) followed by the formation of a liquid sheet twisted in a helix with the subsequent fragmentation of this sheet in ligaments (b). With the increasing pressure, the helix is completely fragmented - even if a small V-shape reminiscent of this structure can still be seen at the base of the injector in (c) - and the atomisation can now progress towards its steady state, i.e. from state (d) to state (e). It is important to note that the picture (e) was taken without the backlight to see more easily the internal structure (hollow cone) of the spray which was achieved with a pressure of 40 bar and a monopropellant throughput of 0.3 mL/s.

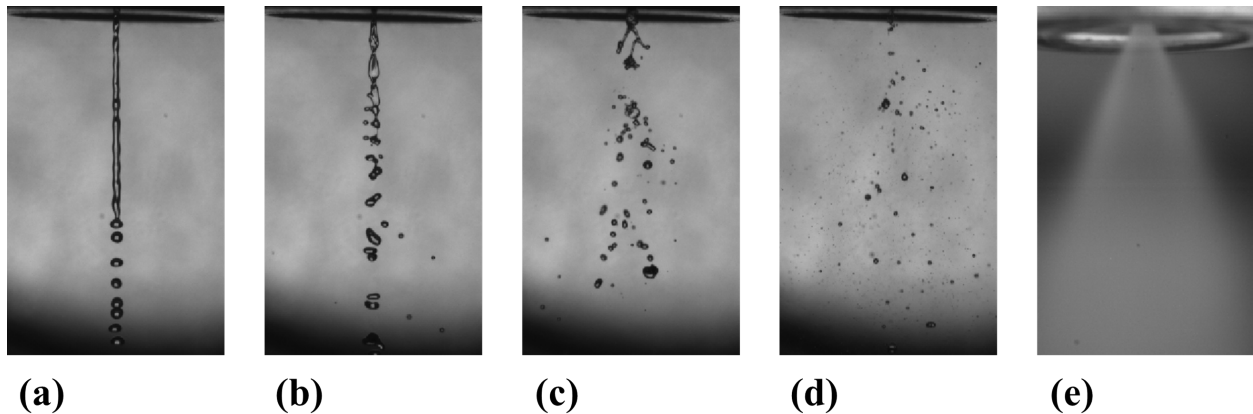


Fig. 15 Growth and evolution of a spray of CNES03 [(a) to (d)] and its steady state (e).

2. Ignition

The ignition test carried out on CNES03 had to visually confirm the decomposition and combustion of the monopropellant. For this, we wanted to film two important moments of the life of the drop: its impact with the hot plate [(a) to (d) in Fig. 16] and the decomposition of one of its residual droplets [(e) to (i) in Fig. 16]. Concerning its impact, we can first see that, after hitting the plate and flattening [(a) and (b)], the droplet starts immediately to emit vast amounts of smoke and fine droplets [(c) and (d)].

After the absorption of the shock, the drop divided itself into several droplets - which had all burned but two by the time of (e). It is extremely important to note that, while no Leidenfrost effect could affect the monopropellant droplets due to their extremely low vapour pressures, the droplets seen in (e) still adopt a round shape and appear to *float* slightly above the hot plate. Such behaviour is believed to come from the emission of gases as in the Leidenfrost effect, except that this emission does not come from the evaporation but from the decomposition of the monopropellant.

When observing the decomposition of the right droplet in the right column of Fig. 16, we can note that after attaining a certain temperature and gradually swelling - certainly due to the internal concentration of decomposition gases - (e), the droplet bursts (upper-right of the right droplet in (f)), fragments itself once more (g) and quickly shrinks (h) before disappearing completely (i).

D. Discussion

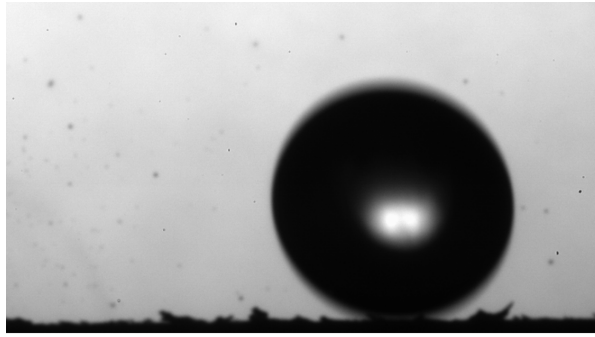
1. Atomisation

We could see in Fig. 15 that atomisation could be reached at 40 bar with CNES03. Let us also remember that this pressure is 20 bar inferior to the optimal pressure of the nozzle (60 bar). It means that the preferred monopropellant - i.e. CNES05 - should be atomised without any major difficulty for the following two reasons : first, CNES05 possesses a surface tension approximately 17% lower than that of CNES03, which means that it should atomise with a lesser required pressure and second, we are able to impose a pressure up to 50% higher than the one used with CNES03 should CNES05 necessitate it. Consequently, we are now willing to continue our efforts towards a future atomisation campaign with CNES05 to map its operating limits and efficiency according to the injection and ambient pressures.

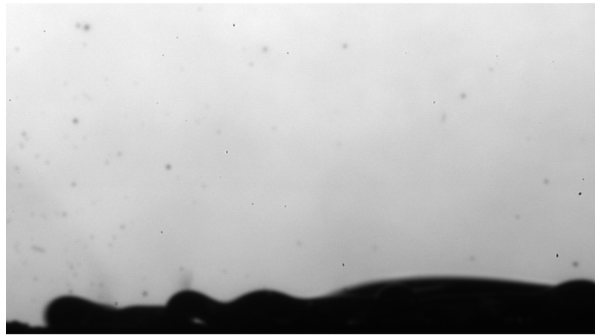
2. Ignition

First of all, it should be noted that the drop that appears in Fig. 16 (a) is much larger than the ones created by atomisation (cf. Fig.15) - with a diameter slightly inferior to 4mm instead of being inferior to 100 μm - and is, as such, not representative of the atomisation granulometry and thus of how a monopropellant droplet coming from the aforementioned spray would burn. This has been done in order to evaluate the ignitability of CNES03 in a worst case scenario (as the temperature of the plate locally decreases more in this case) whilst having a better view of the phenomena unfolding in this experiment. Furthermore, the creation of a single and isolated representative droplet would have required more efforts and have defeated the main purpose of performing these preliminary tests on CNES03 - i.e. sparing costs in equipment, personnel and GMP.

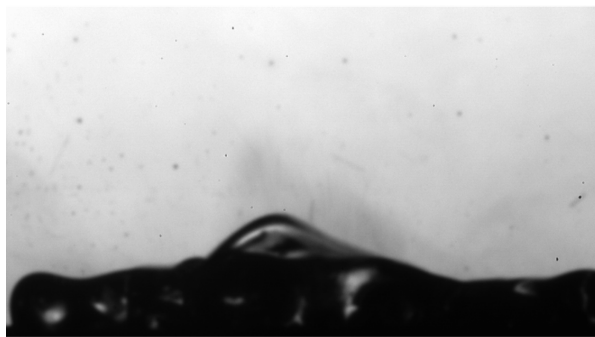
Keeping this in mind, we can now analyse a bit further the results that are illustrated in Fig.16. For images (a) to (d), we can notice that the drop starts to emit a large amount of gases and other much finer droplets. This means that should a larger droplet impact the plate during the combustion of a spray, it may then divide into finer droplets, thus increasing its chances to be burnt. For images (e) to (i) we can see that an equivalent to the Leidenfrost effect probably caused by the decomposition of the monopropellant impedes the sprawl of the drop on the plate which can constitute both a challenge and an asset. Indeed, a reduced contact with the plate will slow down the heating process of the drop thus delaying its combustion, but it will also mean that this bigger drop will decrease the temperature of the plate more slowly and will allow other finer droplets to impact an igniter that might be - thanks to this effect - hot enough to start their combustion, which can, in turn, ignite this first bigger drop. Moreover and concerning the decomposition of the right droplet ((e) to (i)), it appears that the drop exploded under the sheer inner pressure built up by the internal gases of decomposition. However, even if the drop exploded instead of burning, we can nonetheless note that its fragments were consumed rapidly and could be seen shrinking as if they were burning (steady regression rate without the creation of filaments, droplets, etc.). Unfortunately, no gases of combustion could be seen to corroborate this statement which is the reason why we will, in the near future, pursue our research by setting up a more advanced combustion experimental bench for CNES05 that will notably allow us to map the ignition limits based on the plate temperature and the ambient pressure.



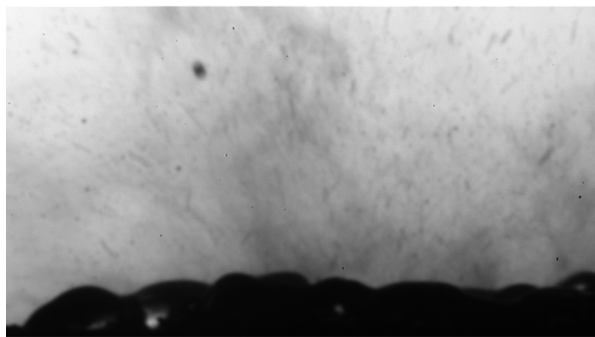
(a)



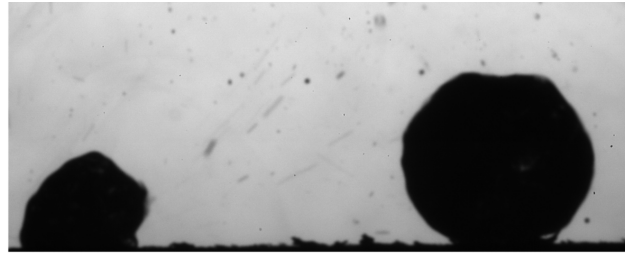
(b)



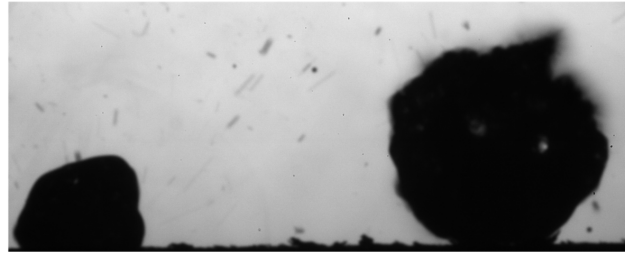
(c)



(d)



(e)



(f)



(g)



(h)



(i)

Fig. 16 Impact (left) and decomposition (right) of a drop of CNES03 on a hot copper plate.

VI. Conclusion

While hydrazine is a monopropellant that has been used for more than half a century, its future prohibition on the European soil by the REACH treaty requires from the aerospace research to find its successor. In this article, we have reviewed the monopropellant candidates that form part of the ONERA / CNES solution.

First, we have analysed their surface tension and have highlighted a reaction between CNES03, ID25 and the brass support that has been confirmed by a material compatibility trial. Also, and for CNES05, we have measured a surface tension approximately 15% lower to that of water at 20°C; a result that encourages us to continue our experiments towards the ignition and atomisation on this monopropellant.

Second, the material compatibility trial has shown that, on top of the two reactions that were suspected during the surface tension tests (CNES03 / Brass and ID25 / Brass), ID25 reacted with stainless steel and CNES05 lightly reacted with brass. Concerning ID25, this sensitivity to stainless steel - a material often used in spacecraft applications - makes it all the more difficult to imagine this monopropellant used in flight which is why it will be forgone in future experiments. Regarding CNES05 and CNES03 we now may explain the curvature of their surface tension evolutions with temperature. Indeed, it appears that the monopropellant that has reacted the most with brass (i.e. CNES03) is also the GMP that has seen its surface tension curve the most when the temperature increased. We can therefore imagine that, with a different support (e.g. in stainless steel), both CNES03 and CNES05 could see their surface tensions follow a linear decrease as was the case with water.

Third, and thanks to these tests on surface tension and material compatibility, we were able to move forward and safely demonstrate the ignitability and atomisation capability of CNES03 which has a surface tension 17% higher than CNES05. These demonstrations, with what has become a test fluid, allowed us to calibrate our test benches and confidently plan the future atomisation and combustion experimental campaign with CNES05 - a GMP that should atomise effortlessly and ignite just as well as CNES03.

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